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A catalytically active porous coordination polymer based on a dinuclear rhodium paddle-wheel unit†

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Two new coordination polymers, DUT-82 and DUT-83 (DUT – Dresden University of Technology), were synthesized by a solvothermal reaction in methanol of rhodium(II) acetate and the tricarboxylic acid H_3btc (btc – benzene-1,3,5-tricarboxylate) or H_3btb (btb – benzene-1,3,5-tribenzoate), respectively. After drying using supercritical carbon dioxide, aerogels with specific surface areas of up to 1150 $m^2\ g^{-1}$ and pore volumes of up to 2.26 $cm^3\ g^{-1}$ were obtained. Although there is no long range order in the materials, the presence of rhodium paddle-wheel units and thus a local order was proven by X-ray absorption spectroscopy measurements. DUT-82 shows good performance in the adsorption of hydrogen and a high affinity for carbon monoxide, which is rarely observed for metal–organic frameworks. Catalytic investigations demonstrate the activity of DUT-82 in the heterogeneous hydrogenation of styrene as a model system. DUT-82 can be recycled for at least ten cycles underlining the stability during the course of reaction.

Introduction

Metal–Organic Frameworks (MOFs) are well known for their excellent properties regarding gas storage and separation as well as catalytic activity along with a rational building block design.[1,2] Using appropriate building blocks, MOFs can be tailored towards the adsorption of special gases[3] or towards certain catalytic reactions.[4] A very important role in the creation of specific interaction points is the secondary building unit (SBU), as many catalytic reactions proceed at the metal centers involved in the framework formation.[5] Also adsorption is influenced by the presence and density of certain metal sites.[6] Not only the choice of the metal is crucial but also its local environment, *e.g.* open metal sites *vs.* a closed coordination shell of the metal.[7] Nevertheless there are only a few examples of MOFs based on noble metals, although they exhibit outstanding properties, *e.g.* their catalytic activity. A noble metal that seems to be promising for the integration into MOFs is rhodium. On the one hand it shows good catalytic activity in various reactions, like hydrogenations[8] and hydroformylations,[9] on the other hand it shows structural features typical for MOF chemistry. Rhodium(II) acetate consists of a paddle-wheel unit,[10] a structural motif often observed in MOFs, *e.g.* in the well studied HKUST-1 (HKUST – Hong Kong University of Science and Technology).[11]

In previous years a number of coordination polymers based on diisocyano ligands and ruthenium,[12,13] palladium,[14,15] platinum,[14,15] iridium[16] and rhodium[16,17] were prepared and their catalytic activity was investigated. In 2006, Navarro *et al.* reported on the compound $[Pd(2\text{-pymo})_2]_n$ (pymo = 2-pyrimidinolate) and thus the first MOF based on palladium. They investigated gas adsorption properties and observed a high thermal stability of $[Pd(2\text{-pymo})_2]_n$.[18] The same group studied also the influence of the functionalization on the gas adsorption properties of $[Pd(2\text{-pymo})_2]_n$.[19] Corma *et al.* showed that $[Pd(2\text{-pymo})_2]_n$ is a versatile catalyst in the Suzuki–Miyaura cross-coupling as well as hydrogenation and oxidation reactions.[20] Further catalytic studies were undertaken by Opelt *et al.*[21] It was shown that palladium black formation takes place during the course of the catalytic reaction. To create active heterogeneous catalysts, the incorporation of palladium precursor solutions into MOFs exhibiting a large pore volume like MOF-5 and MIL-101 (MIL – Matériaux Institut Lavoisier) followed by the formation of nanoparticles has also been intensively studied.[22–25] For example, Pd@MIL-101 shows good activity in the hydrogenation of styrene and *cis*-cyclooctene.[26] Mori *et al.* have carried out some pioneering work in the field of coordination polymers based on noble metals such as ruthenium and rhodium and porphyrin, terephthalate or fumarate as ligands.[27–29] The resulting coordination polymers showed catalytic activity in hydrogen exchange reactions as well as hydrogenation reactions. In 2012 Mori *et al.* integrated a rhodium

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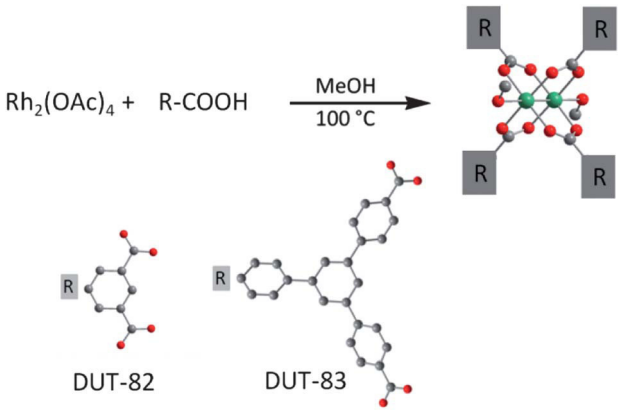
paddle-wheel unit into a bimetallic MOF containing rhodium and copper or zinc, respectively.[30]

One possibility to generate a 3D network is to interconnect the paddle-wheel unit with a tritopic linker.[31] Combination of paddle-wheel units with tritopic linkers like trimesate (btc^{3-}) or benzene-1,3,5-tribenzoate (btb^{3-}) gives MOFs, like the well studied HKUST-1 ($Cu_3(btc)_2$),[11] the molybdenum based analogue TUDMOF-1,[32] the interpenetrated coordination polymer MOF-14 ($Cu_3(btb)_2$),[33] the non-interpenetrated pendant MOF-143 (ref. 34) or DUT-34,[35] respectively, and many other MOFs.[36] In 2011 Fischer *et al.* synthesized the first MOF based on trimesate and ruthenium as noble metal.[37]

In this work, we report the synthesis as well as adsorption and catalytic properties of two novel porous coordination polymers DUT-82 and DUT-83 based on a dinuclear rhodium paddle-wheel unit and tritopic linkers btc^{3-} and btb^{3-}.



Scheme 1 DUT-82 and DUT-83 are synthesized in a solvothermal reaction over a period of five days.

Results and discussion

Synthesis

DUT-82 and DUT-83 gels were synthesized by a ligand exchange reaction between $Rh_2(OAc)_4$ and $H_3(btc)$ or $H_3(btb)$, respectively in methanol (MeOH) as solvent (Scheme 1).

Solvent, rhodium precursor, and synthesis temperature play a crucial role in the product formation: (i) Most of the solvents tested such as ethanol, *N*,*N*-dimethylformamide, *N*,*N*-diethylformamide or water cause at least a partial reduction of rhodium to rhodium black rather than a gelation; (ii) the precursors tested can be divided into two types. One group includes substances already containing a paddle-wheel fragment; and the second group containing different structural features. Trials with precursors of the second group lead either to rhodium black formation ($RhCl_3$) under the selected reaction conditions or to no gel formation ($Rh_4(CO)_{12}$) not only in methanol but also in a variety of solvents. The precursors containing a paddle-wheel unit such as rhodium(II) acetate and rhodium(II) trifluoroacetate have the advantage of containing rhodium in the desired oxidation state and a preformed SBU. In the case of preformed SBU, one can take advantage of the so-called controlled SBU approach; (iii) higher temperature (*e.g.* 160 °C for 3 h) causes the formation of rhodium black impurities, even by the reaction with rhodium(II) acetate in methanol.

The compounds synthesized under optimized conditions (see Section 2 of ESI† for more details) were dried using supercritical carbon dioxide yielding turquoise powders (Fig. S1†). The solvent molecules coordinated to the axial position of paddle-wheels remain during the supercritical drying and were removed by additional activation of the materials at 150 °C under dynamic vacuum.

This process is accompanied by a color change from turquoise to bright green (Fig. S1†). The X-ray diffraction (XRD) patterns of DUT-82 and DUT-83 show no peaks (Fig. S2†), indicating the lack of long range order of the compounds. Also peaks of rhodium were absent.

The coordination environment of the rhodium atoms in the coordination polymers plays a crucial role for the origin/absence of catalytic activity of the material. In order to get information of the local environment of the rhodium atoms, XAS (X-ray Absorption Spectroscopy) measurements of the rhodium K-edge were performed on DUT-82. Comparison of rhodium(II) acetate (Fig. S5†) and DUT-82 spectra shows the presence of dinuclear rhodium paddle-wheels as SBU in DUT-82 (Fig. 1). Thus, the reaction of rhodium(II) acetate and trimesic acid can be seen as a ligand exchange reaction with the rhodium paddle-wheel unit remaining intact.

Thermogravimetric measurements (Fig. S7 and S8†) indicate a thermal stability up to 250 °C for DUT-82 and DUT-83, which allows an additional thermal activation after drying with supercritical carbon dioxide. Elemental analyses indicate that the rhodium paddle-wheel unit is not solely coordinated by the tritopic ligand, but obviously by a mixture of tricarboxylate and acetate ligands (see Section 6 of ESI†).

Gas adsorption properties

The porosity of the compounds was proven first by nitrogen adsorption at 77 K. Thermal activation in vacuum leads to nonporous phases. However, after drying with supercritical carbon dioxide, DUT-82 and DUT-83 exhibit permanent porosity. Supercritically dried DUT-82 has a BET (Brunauer–Emmett–Teller) surface area of 420 $m^2\ g^{-1}$ (Fig. S10†). Further

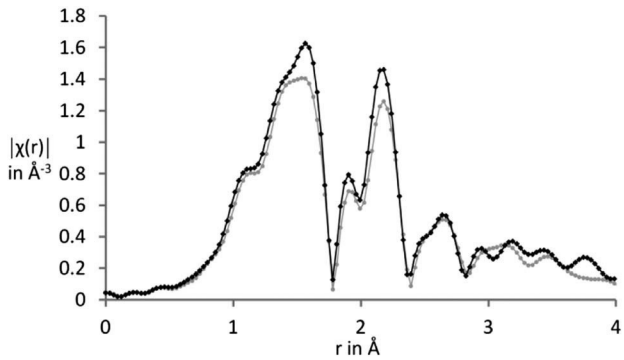


Fig. 1 Radial distribution of atoms around rhodium in DUT-82 (grey) and $Rh_2(OAc)_4 \cdot 2MeOH$ (black) calculated from XAS data at the rhodium K-edge.

activation under vacuum at room temperature improves the adsorption properties. Finally the highest nitrogen uptake is obtained when the supercritical drying is followed by a thermal activation at 150 °C for 16 h. After such treatment, DUT-82 has a BET specific surface area of 780 $m^2 g^{-1}$ and a total pore volume of 1.64 $cm^3 g^{-1}$ (Fig. 2).

The shape of the isotherms is typical for aerogels.[38] According to IUPAC classification the isotherms are of type IV, which is characteristic for mesoporous materials possessing high micropore volume. The micropore volume is 0.37 $cm^3 g^{-1}$ for DUT-82 and 0.54 $cm^3 g^{-1}$ for DUT-83. The hysteresis loop in the regime of mesopore filling of the isotherms (Fig. S10†) corresponds to type H2 and is generally considered as the signature of a disordered porous material with a wide distribution of the pore size. The pore size distribution calculated from nitrogen physisorption reveals only a defined maximum for micropores with the diameter of 12 Å and a broad distribution in the mesopore range (Fig. S11†).

DUT-83 displays a similar shaped isotherm with a higher uptake compared to DUT-82. The specific surface area of DUT-83 is 1150 $m^2 g^{-1}$ and the total pore volume 2.26 $cm^3 g^{-1}$, which is, to the best of our knowledge, the highest value reported for rhodium based MOFs.

Hydrogen physisorption measurement at 77 K on DUT-82 reveals an uptake of 2.2 wt% at 1 bar (Fig. S12†), which is almost identical with the value for crystalline HKUST-1.[39] The adsorption capacity of DUT-82 for carbon dioxide is 138.7 $cm^3 g^{-1}$ (21.4 wt%) at 196 K and 42.8 $cm^3 g^{-1}$ (7.7 wt%) at 273 K, respectively.

Capturing or adsorbing carbon monoxide is of interest due to the high toxicity of the gas. Nevertheless, a considerable adsorption capacity for carbon monoxide at room temperature is rarely observed for MOFs.[40] Interestingly, carbon monoxide adsorption does not only depend on the presence of open metal sites in a MOF, *e.g.* HKUST-1 shows no considerable adsorption, but also on the type of metal, density of open metal sites, and pore dimensions. CPO-27-Ni[41] and rhodium based DUT-37 (ref. 42) are able to adsorb a significant amount of carbon monoxide. The affinity of DUT-82 towards carbon monoxide was investigated by typical sorption and breakthrough experiments at various temperatures. At 77 K DUT-82 shows an isotherm with similar shape and uptake compared to the nitrogen adsorption isotherm (Fig. 3). In contrast, there is a hysteresis in carbon monoxide adsorption/desorption isotherms indicating that carbon monoxide cannot be completely removed from the sample by pressure reduction. Even at room temperature DUT-82 shows a type I carbon monoxide adsorption isotherm and corresponding hysteresis (Fig. 4). These observations are further supported by breakthrough measurements (Fig. S16†). After the first cycle the breakthrough time drops to a constant level for the second and third cycle. Infrared (IR) measurements performed on samples used for carbon monoxide adsorption experiment also reveal that some carbon monoxide is captured by DUT-82 (band at 2080 cm^{-1} in the IR spectra can be associated with bound carbon monoxide) and cannot be removed under vacuum at room temperature (Fig. S18†), but under vacuum and additional heating to 150 °C. The carbon monoxide adsorption isotherms were additionally collected at 273 K, 258 K, and 77 K (Fig. S14†). Unfortunately, the apparatus used for the measurements is not able to resolve the isotherm in the low coverage regime, thus the isosteric heat of adsorption at low coverage could not be calculated. The heat of adsorption at 1.7 mmol g^{-1} carbon monoxide loading is about 50 kJ mol^{-1} and decreases drastically with increasing uptake down to 6 kJ mol^{-1}. Also several runs of carbon monoxide adsorption/desorption were performed on the same sample at 77 K (Fig. S17†). Between the measurements the sample was activated in vacuum at elevated temperature. The uptake decreases slightly from run to run, but not significant, so that drastic degradation of the material can be excluded.

Catalysis

According to the structural investigations, DUT-82 consists of dinuclear rhodium paddle-wheel units offering open metal sites

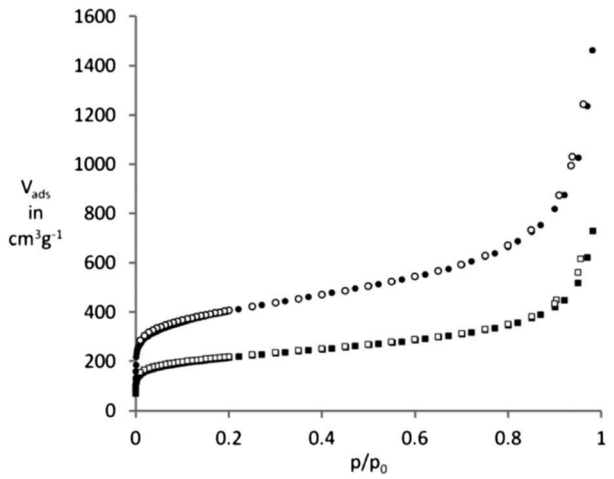


Fig. 2 Nitrogen physisorption isotherms measured at 77 K for DUT-82 (solid squares adsorption, open squares desorption) and DUT-83 (solid circles adsorption, open circles desorption).

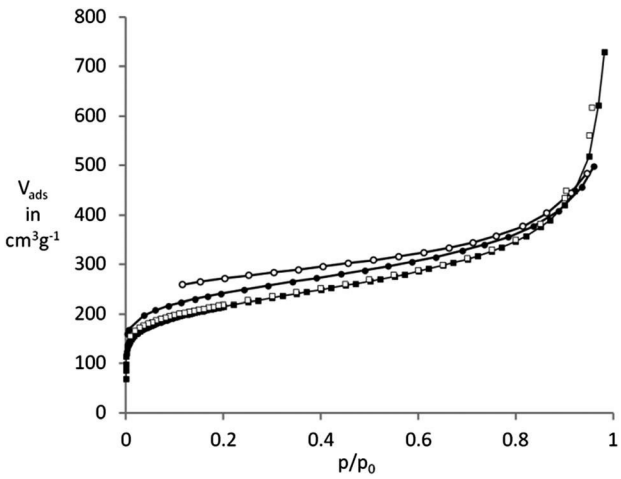


Fig. 3 Nitrogen physisorption isotherm (solid squares adsorption, open squares desorption) and carbon monoxide adsorption isotherm (solid circles adsorption, open circles desorption) measured at 77 K for DUT-82 (p_0 for CO 0.59 bar).

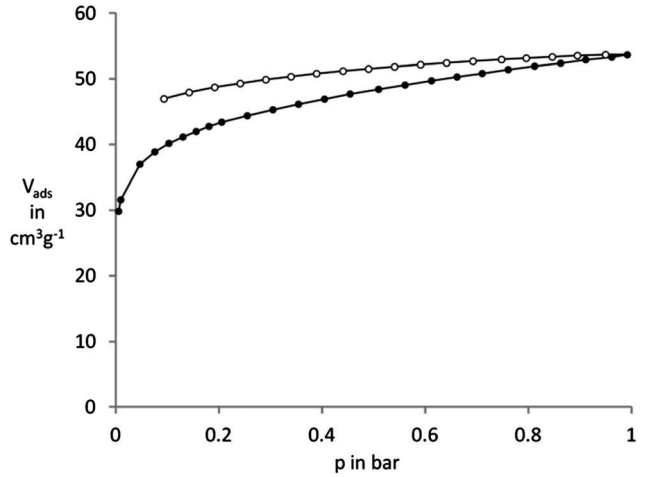
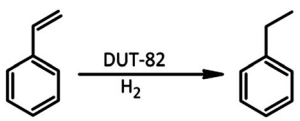


Fig. 4 Carbon monoxide adsorption isotherm measured at 298 K for DUT-82.

after activation. Rhodium(II) acetate is known to be a versatile homogenous catalyst for a range of reactions including hydrogenation,[43] oxidation,[44] cyclo-propanation[45] and C–H insertion.[46] DUT-82 and DUT-83, respectively, are solid porous materials containing the same paddle-wheel building unit and could be considered as heterogeneous pendant to rhodium acetate. Therefore the catalytic activity was tested using hydrogenation of styrene as a model reaction.[47]

Indeed, DUT-82 acts as a catalyst in the hydrogenation of styrene to ethylbenzene (Scheme 2) in *n*-heptane in a hydrogen atmosphere (at 1 bar). The reaction proceeds up to full conversion without the formation of any side products. Using 10 mol% DUT-82 (3.5 mol% rhodium) full conversion to ethylbenzene is achieved within 150 min. Heterogeneity of the reaction mechanism was proven as no further increase of ethylbenzene concentration was observed after removing the catalyst from the reaction solution (for more details see Section 13 of ESI, Fig. S19†). To demonstrate cycle stability of DUT-82, ten consecutive catalysis cycles up to 100% conversion were performed with the same sample of DUT-82. After the tenth cycle the absence of elemental rhodium in the catalyst was proven by XRD measurement (Fig. S21†). However, due to the limited sensitivity of the method we cannot completely rule out the formation of rhodium metal traces.

To further underline the stability of DUT-82 under the selected catalysis conditions, the porosity of a DUT-82 sample was investigated after one and ten catalytic cycles. The solvent in the pores of the sample was exchanged against methanol followed by supercritical drying. Comparison of the adsorption data of the catalyst used with an *as made* sample of DUT-82 reveals the same shape of the isotherm along with a slightly lower uptake of nitrogen for the sample after one reaction run. After ten catalytic cycles, the micropore volume of the catalyst decreases to *circa* one-half of its initial value (0.19 $cm^3\ g^{-1}$) (Fig. S20†).



Scheme 2 Hydrogenation of styrene to ethylbenzene catalyzed by DUT-82.

Conclusions

We have synthesized two new coordination polymers, namely DUT-82 and DUT-83, consisting of rhodium paddle-wheel units being interconnected by tritopic carboxylates. After drying with supercritical carbon dioxide, materials with specific BET surface areas of up to 1150 $m^2\ g^{-1}$ were obtained. DUT-82 is able to capture carbon monoxide with high affinity, which is rarely observed for coordination polymers. Catalytic tests reveal the ability of DUT-82 to act as a heterogeneous catalyst in hydrogenation of styrene to ethylbenzene under 1 bar hydrogen pressure showing good cycle stability at least up to ten cycles.

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